126/263.03

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C09K 5/06

A1

(11) International Publication Number: WO 87/ 07630

(43) International Publication Date: 17 December 1987 (17.12.87)

(21) International Application Number: PCT/GB87/00389

(22) International Filing Date: 4 June 1987 (04.06.87)

(31) Priority Application Number: 8613520

(32) Priority Date: 4 June 1986 (04.06.86)

(33) Priority Country: GB

(71) Applicant *(for all designated States except US)*: EDECO HOLDINGS LIMITED [GB/GB]; 24 Haymarket, London SW1Y 4DG (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : MATTHEWS, Andrew, James [GB/GB]; 112 Paisley Road, Southbourne, Bournemouth, Dorset BH6 5EE (GB). GLOVER, Deborah, Elaine [GB/GB]; 4A Chatsworth Road, Bournemouth, Dorset BH8 8FW (GB).

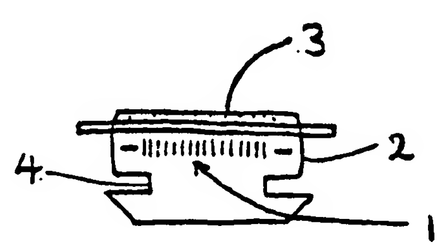
(74) Agent: BOWLES, Sharon, Margaret; S.M. Bowles & Co., Broadway House, London Road, Bourne End, Hemel Hempstead, Hertfordshire HP1 2RU (GB).

(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FI, FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US.

Published
With international search report.

(54) Title: ACTIVATION OF PHASE CHANGE MEDIUM

see page 4
Electromagnetic link



(57) Abstract

An actuator for inducing phase change to a lower temperature phase in a salt hydrate that exhibits a transformation from a high temperature phase to a low temperature phase at a transition temperature. The actuator comprises a coiled spring that is flexed to induce nucleation, a piezoelectric vibration or a thermoelectrically induced cold spot.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

ACTIVATION OF PHASE CHANGE MEDIUM

This invention relates to activation of phase change energy storage media.

There has been much recent interest in utilising the latent heat of phase changes, most notably between different hydrated states of salt hydrates. The latent heat can be regarded as stored while the material is in the upper temperature phase, and this stored energy is released when the transformation to the lower temperature phase occurs. The transition from one phase to the other occurs, with corresponding absorption or release of heat, at the transition temperature. Various salt hydrates have transition temperatures within the range of 0 to 100°C, one of the most favoured being sodium acetate that has a transition temperature of 58.4°C.

A development from investigations of these materials has been the stabilisation of supercooling phenomena in phase change materials in order to produce media that contain a phase change material in the higher energy state but supercooled below the transition temperature so that the latent heat of the transition can be 'stored' at ambient temperatures. In order to stabilise the supercooled state various additives may be included with the phase change material. For example sodium acetate in aqueous solution will undergo a transformation from an anhydrous or less hydrated phase to a more hydrated phase, and if the solution is made very dilute then it can be supercooled well below the normal transition temperature. A more efficient medium, that is with a greater

proportion of phase change material, is described in our United Kingdom patent 2134532 in which a polysaccharide additive stabilises the supercooled state.

Once a phase change material is supercooled it is necessary to have methods of inducing the phase change that are reliable over many cycles, and preferably convenient to use. Dilute solutions of sodium acetate have been found to respond well to activation by snap deformable discs immersed in the solution, the discs being provided with apertures or slits which appear to act as nucleation sites as the disc is snapped. However when these discs are subjected to repeated use they become unpredictable, often becoming more sensitive and causing nucleation for decreasing levels of manipulation with increasing number of snap cycles and yet at other times ceasing to create nucleation until subjected to vigorous and repeated snapping, after which they may become effective again but at a different sensitivity level. Neither the reason for the variation in behaviour nor the basic mechanism of nucleation is understood.

Latent heat storage appliances may take many forms varying from sachets of heat storage medium to complete central heating systems, and even the sachets have many uses varying from simple handwarmers to medical and lifesaving equipment. In some applications such as a hand warmer it may be acceptable to utilise an activator that is a little erratic or requires repeated manipulation, but for more high technology applications involving remote or automatic triggering of nucleation a variation in the sensitivity of the nucleation activator can create problems with control circuits and increase complexity. For example in the event of failure to initiate activation a repeat signal has to be

given and the mechanism has either to have a back up activator or be able to cope with varying sensitivity. On the other hand if an actuator has become over sensitive accidental triggering can occur by shock, such as knocking or dropping the appliance, and this can have very serious consequences if for example a life saving or medical appliance is rendered useless due to premature and unnoticed nucleation.

The present invention is directed towards the provision of consistent activation means. The invention may also be utilised in conjunction with non-supercooled media in systems operating without supercooling in order to ensure consistent or uniform nucleation, or indeed to inhibit supercooling.

Accordingly the present invention provides apparatus for inducing phase change to a lower temperature phase in a salt hydrate that exhibits a transformation from a high temperature phase to a low temperature phase at a transition temperature, the salt being in the higher temperature phase and at or below the transition temperature, the apparatus comprising a coiled spring capable of flexure.

The invention is now described by way of example with reference to the accompanying drawings in which:

Figure 1 shows a spring for use in a first embodiment of the invention;

Figure 2 is schematic cross section through the first embodiment;

Figure 3 is a perspective view of a second embodiment of the

invention, and

Figure 4 is a perspective view of a fourth embodiment of the invention.

In one aspect of the present invention nucleation of latent heat storage appliance is instigated by flexing a coiled metallic spring that is immersed in the medium within the appliance. The medium is preferably sodium acetate trihydrate, most preferably suspended in a xanthan gum gel without a great excess of water. The spring may be flexed manually by manipulation through a flexible portion of the casing or housing of the appliance or the spring may be remotely flexed for example through a mechanical or electromagnetic link. The spring may be made of a variety of materials chosen to suit the medium, expected lifetime and sensitivity requirement of the heat storage appliance. For a sodium acetate based storage medium the following materials may be used for the spring: carbon and alloy steels, copper and copper alloys, stainless steels, nickel alloys and titanium alloys.

If a ferrous metal is used, e.g. carbon steel, then the spring will rust which may lead to contamination of the storage medium and creation of spontaneous nucleation sites. For this reason stainless steel and titanium or nickel alloys are preferred, the latter being especially suitable if highly sensitive activators are required, that is activators that reliably induce nucleation for very small flexure.

The structure of the spring may vary from a tightly wound helical structure in which each turn touches or almost touches its adjacent turns to a looser structure in which the

spaces between turns is greater than the wire diameter or a helix in which the diameter varies between turns.

Figure 1 shows a tightly wound helical spring which may for example be made from circular section wire of diameter 1mm wound to an outside diameter of 3.75mm and having an overall length of about 30mm. With this structure which is of generally elongate format the spring is most easily flexed laterally. Whilst it is possible to provide a spring activator that is free within the body of a container of storage medium and operable by manipulation through a flexible portion of the container, such as is possible if the medium is encapsulated in a flexible plastics sachet, it is generally preferred to locate the activator in a housing to minimise the risk of accidental flexure of the spring by handling the appliance. Preferably the spring is located in a rigid or near rigid housing such as that shown in Figure 2 having a window of more flexible material through which the spring can be deformed. The housing which contains phase change material that is contiguous with the main body of phase change material to be activated, serves to protect the spring from accidental flexure, to positively locate the spring and to retain it in the position most favourable for consistent performance.

Conveniently the housing for the spring may be combined with a port through which phase change material is introduced into its container. Such a port is shown in Figure 2, a side wall 2 forming a housing for spring 1 and an upper flexible seal 3 serving to close the port after filling is complete (the port itself also being full) and provide the flexible window through which the spring 1 can be flexed. It will be noted that the spring ends are supported on inward projections 4

and thus when pressed from above (as viewed) essentially three point bending occurs and the spring is flexed laterally. The activator and housing shown is primarily intended for manual operation although the flexure of the spring could be done automatically, for example utilising a solenoid.

It is possible to utilise configurations of spring other than that shown in Figure 1. For example a looser coil may be used or one having varying turn diameters to form a spiral or other non-uniform structure. If the coil is flat, that is having a diameter of the same order as or greater than the length the spring, it may be flexed by longitudinal pressure, this being aided by having a less closely wound configuration. It should be noted that the longitudinal compression may be applied to the complete spring or to one side. The cross section of the wire from which the springs are formed need not be circular and may be a composite material, single or multi stranded. It has been found preferable to utilise springs of elongate format having relatively tightly wound configurations in which each turn touches a part of the adjacent turn. The sensitivity of the activator in terms of movement required to induce nucleation can be selected by choice of tightness of the coil and ratio of wire diameter to coil diameter. In general increasing the ratio of wire diameter to coil diameter increases sensitivity (less flexing required) as also does tighter winding.

Pre-stressing the spring can also influence the sensitivity and a particularly preferred configuration is an elongate helical coil having a preformed core member that holds the spring in a bent configuration. The greater the degree of bending the greater the sensitivity. If the spring is held in

a U shape by the core the movement for inducing nucleation is imparted by urging the ends of the U closer together. Another structure of interest is a spring that is closed into a loop without free ends, squeezing opposite sides of such a loop towards each other provides the required flexure. The closed loop has the particular advantage that it eliminates free ends that can otherwise be relatively sharp ends that could puncture the container, and for this purpose it is particularly favoured for use within sachets when the activator is not retained in a housing.

With mechanical actuation such as that described with reference to Figures 1 and 2, there is always a chance of accidental triggering. In order to avoid this chance, and also for use with larger or more sophisticated apparatus when manual activation would not be appropriate, electrical operation is preferred. This may be achieved with an electromechanical link to the spring mechanism or by utilising the electrical excitation to induce activation in some other way so that the system is fail-safe in the sense of no electrical excitation, no activation.

Figure 3 shows, schematically, a piezo-electric crystal 6 and its associated power supply and drive circuit 7. The power supply comprises a 1.5V DC source and may be provided by a small battery such as those used in hearing aids or watches and the drive circuit includes an AC/DC converter and frequency multiplier. The crystal 6 is subjected to an oscillating electric field, typically of a frequency of around 20 to 50 KHz bu may be up to 100KHz, which sets up an ultrasonic vibration in the crystal, one face of which is arranged to contact the body of phase change material that is to be triggered. In the embodiment of Figure 3 the power

supply and drive circuit are completely enclosed in a plastics moulding 8 with the piezo-electric crystal 6 being attached to the moulding 8 by a rubbery polymer 9, with a single surface exposed. Thus the entire device is protected from the environment except for the crystal surface. The moulding may be immersed in phase change material without deleterious effect, part of the moulding being secured to the container for the phase change material, or even fabricated integrally with it. A typical size for the moulding housing the circuitry is 20mm x 10mm x 10mm.

In another embodiment the piezoelectric oscillation is transmitted to the phase change material via a point. This may be achieved by an elongate finger or needle of zirconium titanate ceramic projecting into the phase change medium or a needle of another material may be attached to the rectangle to provide a sharper point. The finger may have a cross section of the order of $1mm^2$ and have an aspect ratio of the oreder cf 5:1. This type of assembly may also be protected by a covering.

A third method of activating supercooled phase change material is by inducing a localised temperature gradient by forming a ´cold spot´. Figure 4 shows a third embodiment of the invention in which power circuitry 11 for a Peltier effect device 12 is housed in a moulding 13. The Peltier device 12 may optionally be mounted on a metal insert 14, which acts as a heat sink, and the cold face of the device is exposed. This device is be mounted with the cold face in contact with the phase change material, or in contact with a part of the container wall that is sufficiently thermally conductive to enable a sufficient thermal gradient to be set up. In order to set up a gradient sufficient to induce

nucleation a current through the Peltier element of the order of 100mA to 10A is used which causes a temperature drop of about 70°C within a few seconds. In a preferred embodiment the Peltier device consists of a p-n thermoelectric heat pump. A device of this nature having ceramic faces suitable for contact with the phase change material and with a face cross section of $4mm^2$ and a thickness of 3mm has a pumping capacity of about 0.3 Watts and can be run directly from a small 1.5 V battery. A thermally conductive point may be used to project into the phase change medium to induce a cold spot.

It will be ralised that with both the piezoelectric nucleation and the thermoelectric nucleation activators it is not necessary for the devices to be in actual contact with the phase change material, all that is required is for the physical effect of the vibration or cold to be transferred to the material, that is for an 'operational' contact, thus the devices themselved can be protected from harmful effects of direct contact.

CLAIMS

1. Apparatus for inducing phase change to a lower temperature phase in a salt hydrate that exhibits a transformation from a high temperature phase to a low temperature phase at a transition temperature, the salt being in the higher temperature phase and at or below the transition temperature, the apparatus comprising a coiled spring capable of flexure.

2. Apparatus according to Claim 1 in which the spring comprises a single strand coil.

3. Apparatus according to Claim 1 in which the spring comprises a plurality of strands.

4. Apparatus according to any preceding claim in which the spring is wound on to a pre-formed core.

5.Apparatus according to any preceding claim in which the spring is a helical spring the turns of which are in substantial contact with adjacent turns.

6. Apparatus according to any preceding claim in which the spring is elongate and adapted to be laterally flexed.

7. Apparatus according to any preceding claim in which the flexure of the spring is remotely controlled.

8. Apparatus for inducing phase change to a lower temperature phase in a salt hydrate that exhibits a transformation from a high temperature phase to a low temperature phase at a transistion temperature, the salt being in the higher temperature phase and at or below the

transition temperature, the apparatus comprising a piezoelectric or thermoelectric device mounted with a surface in operational contact with the salt hydrate.

9. Apparatus according to claim 8 in which the device is powered by battery.

10 Apparatus according to claim 8 or claim 9 in which the device is provided with a point that projects into the salt hydrate.

11. Apparatus according to any preceding claim in which the salt hydrate is sodium acetate trihydrate.

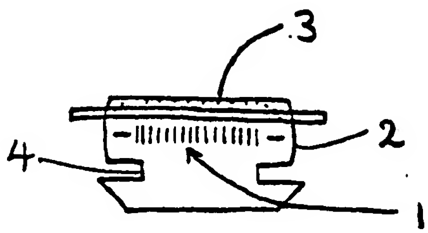


Figure 2

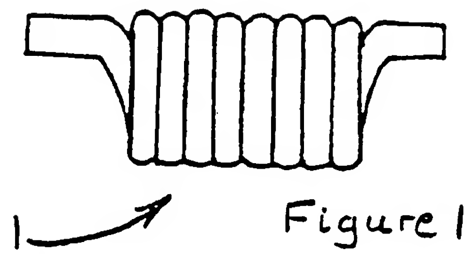


Figure 1

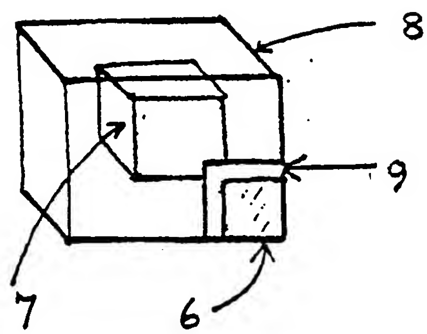


Figure 3

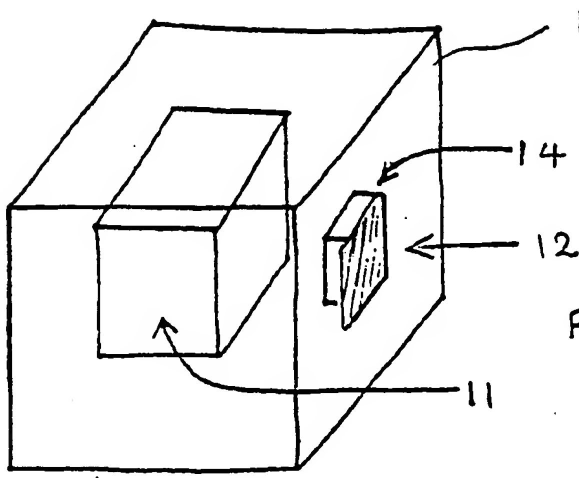


Figure 4

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00389

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 09 K 5/06

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	C 09 K B 01 D F 28 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	DE, A, 3203306 (BERGER) 28 July 1983 see claims 1,2,6; page 6, line 18 --	1,5,8,10,11
X	FR, A, 2494710 (DEUTSCHE FORSCHUNGS- UND VERSUCHSANSTALT FÜR LUFT- UND RAUMFAHRT) 28 May 1982 see claims 1,5 --	8,10
X	US, A, 2876083 (PRIETZ) 3 March 1959 see claim 1; column 1, line 51 --	8
A	DE, A, 2619514 (WERDING) 18 November 1976 see claims 1,8; page 2, line 28; page 7, line 30 - page 8, line 8 --	1,7,11
A	DE, A, 3108760 (IMHOF) 28 October 1982 see claims 1,11 --	1,7,11
A	US, A, 2220777 (OTHMER) 5 November 1940 --------	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
20th July 1987	16 SEP 1987
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 87/00389 (SA 17431)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/07/87

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publicatio date
DE-A- 3203306	28/07/83	None		
FR-A- 2494710	28/05/82	DE-A,C	3044202	27/05/82
		US-A-	4461153	24/07/84
		CA-A-	1183447	05/03/85
US-A- 2876083		None		
DE-A- 2619514	18/11/76	None		
DE-A- 3108760	28/10/82	None		
US-A- 2220777		None		

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

DERWENT-ACC-NO: 1987-362720

DERWENT-WEEK: 198751

TITLE: Reliable phase change activation device - for salt hydrate in latent heat storage system

INVENTOR: GLOVER, D E

PATENT-ASSIGNEE: EDECO HOLDINGS LTD[EDECN] , MATTHEWS A J[MATTI]

PRIORITY-DATA: 1986GB-0013520 (June 4, 1986) , 1987GB-0001170 (June 4, 1987)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
WO 8707630 A	December 17, 1987	E	014	N/A
AU 8774835 A	January 11, 1988	N/A	000	N/A
DK 8800552 A	February 3, 1988	N/A	000	N/A
EP 269689 A	June 8, 1988	E	000	N/A
FI 8800502 A	February 3, 1988	N/A	000	N/A
GB 2198449 A	June 15, 1988	N/A	000	N/A
JP 63503463 W	December 15, 1988	N/A	000	N/A

DESIGNATED-STATES: AU DK FI GB JP NO US AT BE CH DE FR GB IT LU NL SE AT BE CH
DE FR GB IT LI LU NL SE

CITED-DOCUMENTS: DE 2619514; DE 3108760 ; DE 3203306 ; FR 2494710 ; US 2220777
; US 2876083

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO 8707630A	N/A	1987WO-GB00389	June 4, 1987
EP 269689A	N/A	1987EP-0903718	June 4, 1987
GB 2198449A	N/A	1987GB-0001170	June 4, 1987
JP 63503463W	N/A	1987JP-0503425	June 4, 1987

INT-CL (IPC): C09K005/06, F28D020/00

ABSTRACTED-PUB-NO: WO 8707630A

BASIC-ABSTRACT:

A device, for inducing phase change to a lower temp. phase in a salt hydrate which is in the higher temp. phase and is at or below the phase transition temp., comprises either (a) a coiled spring capable of flexure or (b) a piezoelectric or thermoelectric device mounted with a surface in operational contact with the salt hydrate.

USE/ADVANTAGE - The device is used to activate phase change energy storage media, such as sodium acetate trihydrate, and provides consistent activation. The device can also be used in conjunction with non-supercooled media to ensure consistent or uniform nucleation or even to inhibit supercooling. /4

TITLE-TERMS: RELIABILITY PHASE CHANGE ACTIVATE DEVICE SALT HYDRATE LATENT HEAT STORAGE SYSTEM

DERWENT-CLASS: E17 G04 Q78 X25

CPI-CODES: E05-A; E10-C04J; G04-B01;

EPI-CODES: X25-X;

CHEMICAL-CODES:
Chemical Indexing M3 *01*
Fragmentation Code
A100 A111 A200 A960 C710 J0 J011 J1 J171 M210
M211 M212 M213 M214 M215 M216 M220 M221 M222 M223
M224 M225 M226 M231 M232 M233 M262 M281 M320 M411
M424 M510 M520 M530 M540 M620 M630 M740 M781 M903
M904 Q434 Q617 R038
Markush Compounds
198751-E1401-U
Registry Numbers
87140 1286M

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C1987-155384
Non-CPI Secondary Accession Numbers: N1987-271889